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# The catalytic vapor-phase hydrolysis of benzene and toluene

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# THE CATALYTIC VAPOR-PHASE HYDROLYSIS OF BENZENE AND TOLUENE

BY

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A

THESIS

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Assistant Professor of Organic Chemistry.

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C.R.M.

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# INTRODUCTION

The vapor-phase synthesis of organic compounds represents a new field of study which has attracted the attention of investigators only within recent years. However, wide interest is apparent in this field and several processes of commercial importance have already been developed.

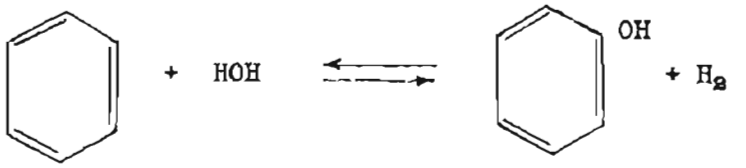
Hydrolysis is perhaps the newest of all the types of vapor-phase synthesis; the literature consists of little more than a few patents. This method of synthesis is of interest because it affords a method of pure hydrolysis (hydrolysis with water alone) for a number of organic compounds which would not otherwise react with water in the liquid-phase.

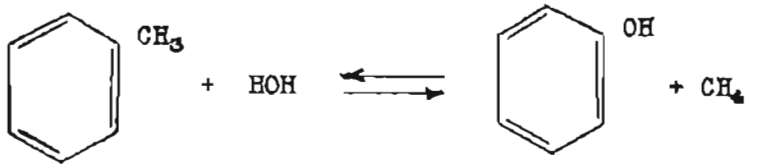
Aromatic hydrocarbons are excellent examples of such substances. Their limited miscibility with water as well as their stability, prohibits any liquid-phase reaction whatever. Vapor-phase reactions on the other hand overcome this limitation by affording more intimate contact between the reactants themselves, and by employing very high temperatures which have an accelerating effect on the reaction.

The vapor-phase hydrolysis of benzene and toluene, therefore, presented an interesting possibility. These two hydrocarbons are considered very stable toward water in the liquid-phase. The purpose of this investigation was to determine to what extent their stability toward water was altered in the vapor-phase.

## HISTORICAL

An extensive search through chemical literature revealed that the only previous work on the hydrolysis of benzene and toluene was that conducted by Fischer, Schrader, and Meyer,[1] and by Lloyd.[2] Fischer, Schrader and Meyer performed experiments in connection with the two following reactions:-

1. 


2. 


Most of their experiments were performed on the first reaction; only two were carried out in connection with the second. All of their experiments were performed with the reacting substances in the vapor state at elevated temperatures.

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1. Fischer, Franz., Schrader, Hans., & Meyer, Wilhelm., Über die Thermische Behandlung Aromatischer Verbindungen (II Teil). Ges. Abhandl. Kenntn. Kohle., Vol. 5, p. 417-419, 1920.

2. Lloyd, S. J., Hydrolysis, Chapter XI, p. 537-74 in: Groggins, P. H., ed., Unit Processes in Organic Synthesis. 1st. ed. New York, N. Y., McGraw-Hill Book Co., Inc., 1935.

In the case of the first reaction, they discovered that equilibrium lies strongly toward the benzene side. This was determined by trying the reaction in both directions.[3] However, they further discovered that this equilibrium condition could be reversed by two methods: by increasing the temperature, and also by increasing the percentage of water in the reaction mixture. 760° to 770° C. was found to be the optimum temperature, and excess of water amounting to about eight times the theoretical quantity necessary was found to give the best yield of phenol.

The second reaction was also tried in both directions. In both cases, however, no detectable amounts were obtained. No phenol was obtained when the reaction was tried toward the right and no toluene was obtained when the reaction was tried toward the left. The investigators believed, nevertheless, that the reaction would proceed in either direction if larger quantities of materials were used and if excess of either water or methane were employed, depending on the direction of the reaction.

Throughout their work Fischer, Schrader, and Meyer[4] used two kinds of reaction tubes, a tinned-iron tube, and a porcelain tube.

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3. Fischer, Franz., The Production of Light Motor Fuels from Low Temperature Coal and Lignite tar, Especially the Conversion of Phenols or Cresote into Benzene. Brennstoff Chem., Vol. 2, p. 327-30, 347-9, 1921; Abstracted in Chem. Abstr., Vol. 16, p. 816, 1922.

4. Fischer, Franz., Schrader, Hans., & Meyer, Wilhelm., Über die Thermische Behandlung Aromatischer Verbindungen (II Teil). Ges. Abhandl. Kenntn. Kohle., Vol. 5, p. 417-419, 1920.

They used small quantities of reactants, usually less than 10 grams, and did not test the effect of catalysts. Phenol was determined qualitatively in all cases by precipitation with bromine water.

S. J. Lloyd[5] confirmed the results of Fischer, Schrader, and Meyer in connection with hydrolysis of benzene. He attempted to increase the yield of phenol in that reaction by the use of various solid catalysts such as chromium oxide, and zinc ferrite, but found that these had little or no effect.

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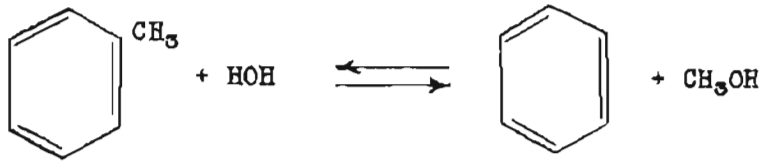
5. Lloyd, S. J., Hydrolysis, Chapter XI, p. 637-74 in: Groggins, P.H., ed., Unit Processes in Organic Synthesis. 1st. ed. New York, N. Y., McGraw-Hill Book Co., Inc., 1935.

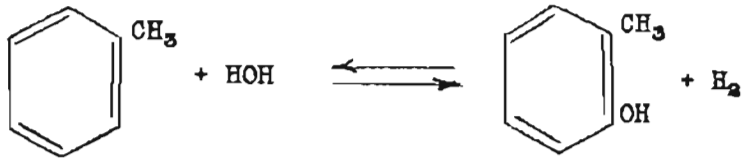
## THE PROBLEM

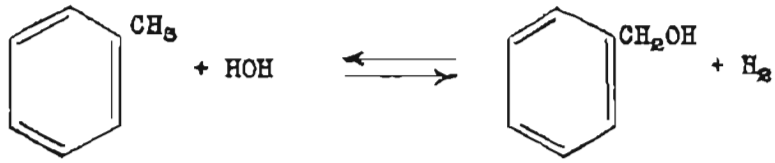
The purpose of this investigation was to extend the work on the hydrolysis of benzene and toluene in the vapor-phase.

The hydrolysis of toluene presents several other possible reactions besides the synthesis of phenol which was considered by Fischer, Schrader and Meyer;[6] these reactions are represented by four equations as follows:-

1. 


2. 


3. 


4. 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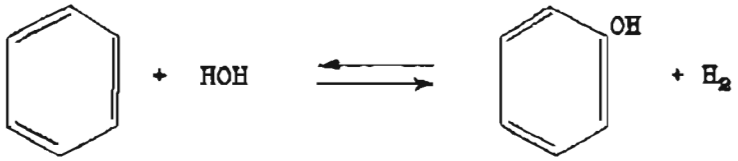
6. Fischer, Franz., Schrader, Hans., & Meyer, Wilhelm., Über die Thermische Behandlung Aromatischer Verbindungen (II Teil). Ges. Abhandl. Kenntn. Kohle., Vol. 5, p. 417-419, 1920.

The hydrolysis of benzene on the other hand presents only one possibility: the phenol synthesis. This is shown by the following equation.




Since the hydrolysis of benzene was more thoroughly investigated by previous experimenters, it was decided to concentrate this investigation on the hydrolysis of toluene, including all of its possible reactions, in order to determine to what extent these took place under the conditions of a given experiment.

It was decided to further extend the work of previous investigators along four lines as follows:-

1. To determine the effect of catalysts.
2. To determine the effect of larger quantities of reactants.
3. To determine the effect of temperature.
4. To analyze for all reaction products quantitatively.

Catalysts as applied to vapor-phase hydrolytic reactions has scarcely any mention at all in the literature. Silica gel catalysts

however, seem to be favored.[7,8,9] It was decided, therefore, to prepare a number of catalysts of that type, and to determine their efficiency in the reactions to be considered.

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7. Chalkley, Lyman, Jr., The Vapor-phase Hydrolysis of Phenol Chloride and Bromide. J. Am. Chem. Soc., Vol. 51, p. 2489-2495, 1929.

8. Tishchenc, D.V., & Churbakov, A.M., Catalytic Saponification of Chlorobenzene with Steam. J. Applied Chem. (U.S.S.R.), Vol. 7, p. 764-9, 1934; Abstracted in Chem. Absts., Vol. 29, p. 2520-2521, 1925.

9. Zangirolami, Angela., Catalytic Transformation of Mesityl Oxide into Acetone. Action of $Al_2O_3$, $ThO_2$, Pumice and Silica Gel. Ann. Chim. Applicata, Vol. 24, p. 347-52, 1934; Abstracted in Chem. Absts., Vol. 28, p. 7245-7246, 1934.

## CATALYSTS

### (Silica Gels)

All of the silica gel catalysts used in this investigation were prepared in the laboratory. Six different gels were prepared; these may be classified into two main types: The metal-oxide impregnated type, and the pure silica type from which all metal-oxide has been extracted.

The technique employed in preparing these gels was based on the methods and findings of Holmes, Sullivan and Metcalf;[10] Holmes and Anderson;[11] Holmes and Elder;[12] and Frazer and Rush.[13]

In preparing the gels the following materials were used:

| | |
|---|---|
| Sodium silicate solution (40° Be. $Na_2O$:$SiO_2$ ratio 1:3) | Heil Corporation |
| $FeCl_3 \cdot 6H_2O$ | Mallinckrodt's, A.R. |
| $NiCl_3 \cdot 6H_2O$ | Baker's Analyzed, C.P. |
| $CoSO_4 \cdot 7H_2O$ | Baker & Adamson, C.P. |
| $CuSO_4 \cdot 5H_2O$ | Baker's Analyzed, C.P. |

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10. Holmes, H.N., Sullivan, R.W., & Metcalf, N.W., Increasing the Internal Volume of Silica Gels by Moist Heat Treatment. Ind. & Eng. Chem., Vol. 18, p. 386-388, 1926.

11. Holmes, H.N., & Anderson, J.A., A New Type of Silica Gel. Ind. & Eng. Chem., Vol. 17, p. 280-282, 1925.

12. Holmes, H.N., & Elder, A.L., The Vapor Adsorption Capacity of Silica Gels as Affected by Extent of Drying Before Wet Heat Treatment and by Temperature of Acid Treatment and Activation. J. Phys. Chem., Vol. 35, p. 82-92, 1931.

13. Frazer, J.W.C., & Rush, R.I., A Study of The Structural Changes in Amorphous Material, Silica Gels. J. Phys. Chem., Vol. 31, p. 1511-1520, 1927.

Although the technique differed slightly in each case, the general method of preparation may be described as follows:

1. Metal-oxide Impregnated Type.

One and one half liters of a two normal solution of ferric chloride (or other salt desired) was added drop by drop with violent stirring to 500 ml. of sodium silicate solution (40° Be.) which had been previously diluted to 10 liters with distilled water.

As the reaction progressed a heavy, colored precipitate collected at the bottom of the vessel. When all of the salt solution had been added, the gel was set aside for 60 hours and allowed to settle. The clear liquid was then decanted, and the heavy sludge filtered through fine cheesecloth supported on coarse galvanized iron screen. The gel was allowed to dry in this improvised tray until the moisture content was reduced to about 60%. The drying was carried out by placing the filter tray in an open window in the sunlight, usually for one week.

At the end of the drying period, the gel was broken up into lumps about one centimeter in diameter, and bottled in a tightly stoppered bottle for about seven days. This procedure caused the gel to sweat and it is believed by Frazer, and Rush[14] to effect a rearrangement of the gel particles to yield a firmer gel structure.

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14. Frazer, J.W.C., & Rush, R.I., A Study of the Structural Changes in Amorphous Material, Silica Gel. J. Phys. Chem., Vol. 31, p. 1511-1520, 1927.

After the sweating process, the gel was freed of soluble salts by placing the gel lumps in a cloth sack and suspending them in boiling water. The water was changed at regular intervals and tested for chlorides or sulfates depending on the salt used as a precipitating agent. When the gel showed no further traces of soluble salts, it was dried in an oven at 150° C. for eight hours. It was then crushed with a mortar and pestle and screened to pass 8 mesh. Particles finer than 20 mesh were discarded.

At this point in the procedure the gel contained impregnated metal hydroxide which is unstable at high temperatures; the tendency being to dehydrate with the formation of the corresponding metal oxide.[15] In order to avoid this dehydration during the process of a given run, the gel to be used as a catalyst was placed in the reaction tube and activated at 500° C. for 12 hours by passing dry air through the gel mass. The gel was then ready for use as a catalyst.

Four gels of this type were prepared using the following salts as precipitating agents:

| | |
|---|---|
| $FeCl_3 \cdot 6H_2O$ | $CuSO_4 \cdot 5H_2O$ |
| $NiCl_2 \cdot 6H_2O$ | $CoSO_4 \cdot 7H_2O$ |

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15. Mellor, J.W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry. New York, N.Y., Longman's, Green & Co., 1922-1937, Vol. 3, p. 132, Vol. 13, p. 777, Vol. 14, p. 569, Vol. 15, p. 385.

2. Pure Silica Gel Type.

This type of gel was prepared in the same manner as the metal-oxide impregnated gel through the completion of the sweating process. After the sweating process the gel was placed in a 1000 ml. beaker and treated with six normal sulfuric acid to remove the impregnated metal hydroxide. The beaker containing the gel and acid was placed on a sand bath, the acid being changed by decantation every 24 hours.

When the gel became perfectly white and chalky in appearance, the acid leaching process was discontinued and the gel was washed free of sulfates, dried, crushed, and screened in the same manner as the other type of gel. Since this type of gel contains only traces of metal-hydroxide, which can be disregarded, it is possible to use a lower activating temperature, usually 175° C. Otherwise the method used was the same as that previously described.

Two pure silica gels were prepared, one using $FeCl_3 \cdot 6H_2O$ and another using $NiCl_2 \cdot 6H_2O$ as precipitating agents.

The sorption characteristics of a silica gel depend to a great extent on such variables as settling time, drying time, percent moisture at the end of the drying period, and sweating time. Table 1 lists these factors for each gel prepared.

(Other Catalysts)

Beside the silica gels, three other kinds of catalysts were used in the experiments: activated alumina, cast iron drillings, and magnetic oxide of iron. The activated alumina was donated by the Alumium Ore Co.; the cast iron drillings were obtained from

the school machine shop; and the magnetic oxide or iron was prepared from the iron drillings by oxidation with steam at 500° C.

All were screened to the same particle size as the silica gels.

TABLE 1

VARIABLE FACTORS IN THE PREPARATION OF THE SILICA GEL CATALYSTS

Metal-oxide Impregnated Gels

| No. | Precipitating Agent. | Settling Time. | Drying Time. | Moisture % | Sweating Time. |
|---|---|---|---|---|---|
| 1 | $FeCl_3 \cdot 6H_2O$ | 192 hours | 14 days | 52 | 7 days |
| 2 | $NiCl_2 \cdot 6H_2O$ | 64 hours | 3 days | 60 | 8 days |
| 3 | $CuSO_4 \cdot 5H_2O$ | 67 hours | 11 days | 60 | 7 days |
| 4 | $CoSO_4 \cdot 7H_2O$ | 67 hours | 11 days | 50 | 7 days |

Pure Silica Gels

| No. | Precipitating Agent. | Settling Time. | Drying Time. | Moisture % | Sweating Time. |
|---|---|---|---|---|---|
| 1 | $FeCl_3 \cdot 6H_2O$ | 192 hours | 14 days | 52 | 7 days |
| 2 | $NiCl_2 \cdot 6H_2O$ | 64 hours | 3 days | 60 | 8 days |

## PURIFICATION OF BENZENE AND TOLUENE

Benzene and toluene for use in this investigation were each purified in batches of about four liters. In each case the entire batch was vigorously agitated, 500 ml. at a time, with 250 ml. of concentrated sulfuric acid in a separatory funnel.

After the batch had been given four successive treatments in this manner, fresh acid having been used for each treatment, the acid showed no further discoloration. The entire batch was then washed with saturated sodium carbonate solution, then with water, and finally allowed to dry over anhydrous calcium chloride. When the liquid became clear, it was fractionated. The fraction boiling from 110° to 111° C. was collected as toluene. In the case of benzene, the fraction from 80° to 81° C. was collected. A 16 bulb Young distilling column was used in these distillations.

During the purification process about 10% benzene and about 20% toluene were lost due to sulfonation. This loss was kept at a minimum by cooling the liquids with running tap water during the acid treatment.

After the completion of the purification process, the benzene and toluene were tested for thiophene or its derivatives by the indophenin reaction according to Holmes and Beeman.[16] In carrying out this test 25 ml. of liquid was thoroughly shaken

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16. Holmes, H.N., & Beeman, Norvil., Removal of Thiophene from Benzene. Ind. & Eng. Chem., Vol. 26, p. 172-173, 1934.

with 2 ml. of C.P. concentrated sulfuric acid. When the layers separated, 1 ml. of the sulfuric acid layer was drawn off, and to this was added by pipette, 0.1 ml. of a solution of isatin in C.P. concentrated sulfuric acid. (0.4 gram per 100 ml.) This was shaken and allowed to stand. If thiophene or its derivatives are present, a faint greenish yellow color develops with a concentration as low as 0.00035%. When this test was applied to the benzene and toluene purified as described, no thiophene was indicated.

## APPARATUS

Before devising the apparatus, a brief survey was made of the literature in order to determine the kind and variety of apparatus in use among various investigators in vapor-phase reactions,[17, 18, 19, 20, 21, 22] The apparatus used by Chalkley seemed the most suitable;[23] it was therefore adopted, but considerably modified to suit the requirements of this investigation.

Briefly stated, the apparatus consisted of two reservoirs, one for vaporizing benzene, the other for vaporizing water; a reaction tube which held the catalyst, heated by an electric furnace; a condenser; and a receiver in which the reaction products were collected.

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17. Parks, G.W., & Katz, J., Vapor-phase Catalytic Oxidation of Organic Compounds, Toluene. Ind. & Eng. Chem., Vol. 28, p. 319-323, 1936.

18. McKee, R.H., & Wilhelm, R.H., Catalytic Vapor-phase Nitration of Benzene. Ind. & Eng. Chem., Vol. 28, p. 662-667, 1936.

19. Mason, John., Smale, C.A., Thompson, R.N., & Wheeler, T.S., The Thermal Vapor-phase Chlorination of Toluene and Benzene. J. Chem. Soc. (London), p. 3150-3157, 1931.

20. Fischer, Franz., Schrader, Hans., & Meyer, Wilhelm., Über die Thermische Behandlung Aromatischer Verbindungen (II Teil). Ges. Abhandl. Kenntn. Kohle., Vol. 5, p. 417-419, 1920.

21. Cobb, J.W., & Dufton, S.F., Some High Temperature Reactions of Benzene and Toluene. Gas. J., Vol. 150, p. 588-91, 1920.

22. Chalkey, Lyman, Jr., The Vapor-phase Hydrolysis of Phenyl Chloride and Bromide. J. Am. Chem. Soc., Vol. 51, p. 2489-2495, 1929.

23. See foot note 22.

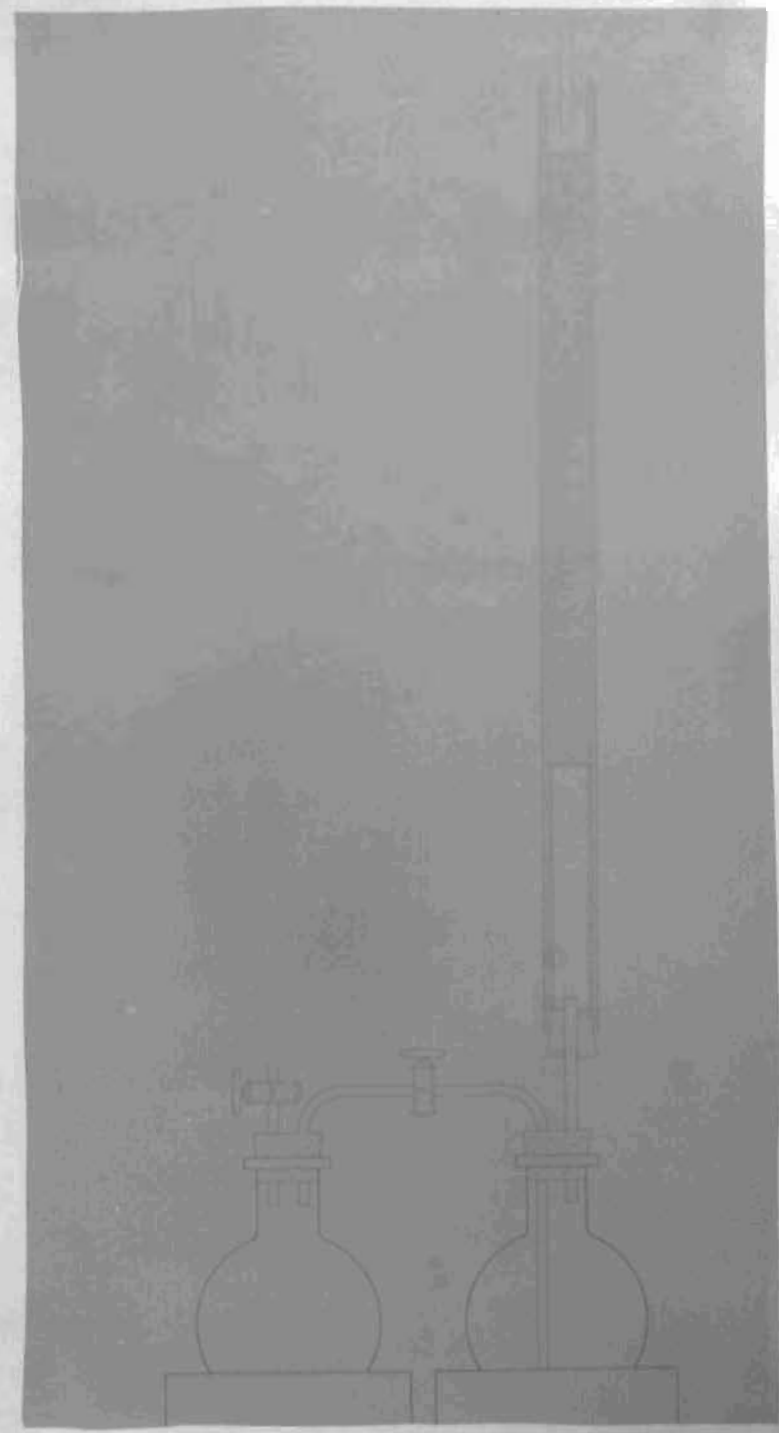

Figure 1. Diagram Showing Reaction Tube in Cross Section.

The reservoirs consisted of two 500 ml. Pyrex, round bottom, short ring neck flasks. These were heated by two Precision electric heaters which were controlled with slide wire rheostats. The flasks were connected by means of a glass tube arranged so that the vaporized benzene bubbled through the boiling water before passing into the lower end of the reaction tube. A stop-cock located at the center of the connecting tube allowed the tube to be closed when desired. The benzene reservoir also contained a second tube with stop-cock which was used to release the pressure within the flask at the end of an experiment.

The reaction tube was connected directly to the water reservoir and consisted of a porcelain tube with an inside diameter of 20 mm., and an outside diameter of 28 mm., and 50 cm. long. The catalyst was supported within the reaction tube on a perforated porcelain disc, (a small filter plate ground down to fit the reaction tube) which was in turn supported by a porcelain cylinder about 15 cm. long. A second perforated porcelain disc was placed on top of the catalytic mass to prevent the particles from blowing over into the condenser tube (see Fig. 1). The reaction tube was heated with a 12 inch Multiple Unit Electric Tube Furnace.

The condenser tube consisted of a piece of 12 mm. glass tubing bent J-shape. The short side was connected to the upper end of the reaction tube; the long side was fitted with a metal water jacket, and was introduced into the receiver (a 750 ml. Erlenmeyer flask).

The receiver was placed inside a glass jar, 14 cm. in diameter and 19 cm. high. This jar contained ice water so that volatile

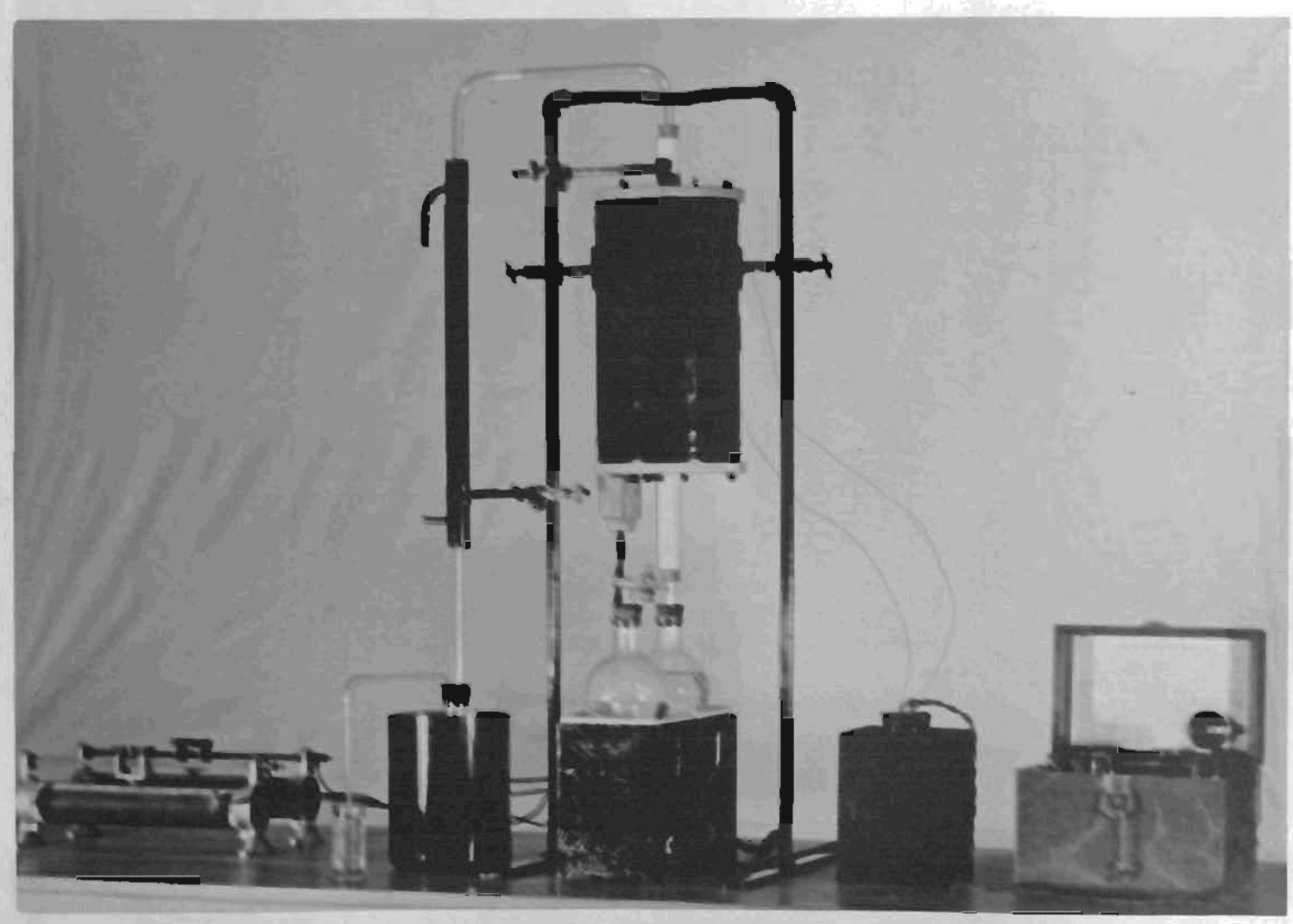

Figure 2. The Apparatus Assembled for an Experiment.

reaction products passing through the condenser unchanged would be liquefied in the receiver. The receiver was also provided with a vent consisting of a small piece of glass tubing which was closed at one end with a water trap (see Fig. 2).

Rubber stoppers were used at all points where gas-tight connections were necessary with the exception of the connections at either end of the reaction tube. It was found that rubber stoppers disintegrated rapidly at these two points due to the high temperature. Cork stoppers were found to be more effective.

The temperature of the furnace was determined and regulated by means of a thermocouple, and two Ward Lenord muffle rheostats connected in series. A chromel-alumel thermocouple was the type used since it gives a large deflection in the temperature range 100° C. to 1000° C. and is also stable within that range. The thermocouple was located within the furnace, just behind the heating element. In order that the thermocouple, in this position, would register the temperature at the center of the catalytic mass (the temperature desired), it was calibrated against a standard rare metal thermocouple (Platinum to Platinum 10% Rhodium) placed within the reaction tube and surrounded with the catalyst.[24] [25] The E.M.F.-temperature curve for the thermocouple thus calibrated is shown in Figure 3.

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24. Foote, P.D., Fairchild, C.O., & Harrison, T.R., Pyrometric Practice. U. S. Bur. Standards, Tech. Paper, No. 170, 1921.

25. Roeser, W.F., & Wensel, H.T., Reference Tables for Platinum to Platinum-Rhodium Thermocouples. U. S. Bur. Standards, J. Res., Vol. 10, p. 275-287, 1920.

Figure 3. Chromel-Alumel Thermocouple Calibration Curve.

It is not to be inferred that the thermocouple as calibrated gives an accurate reading of the temperature at the center of the catalyst. This cannot be obtained because of the temperature lag between the two points. However, with a constant flow of gases and constant current supply to the furnace, fairly reliable readings should be obtainable.

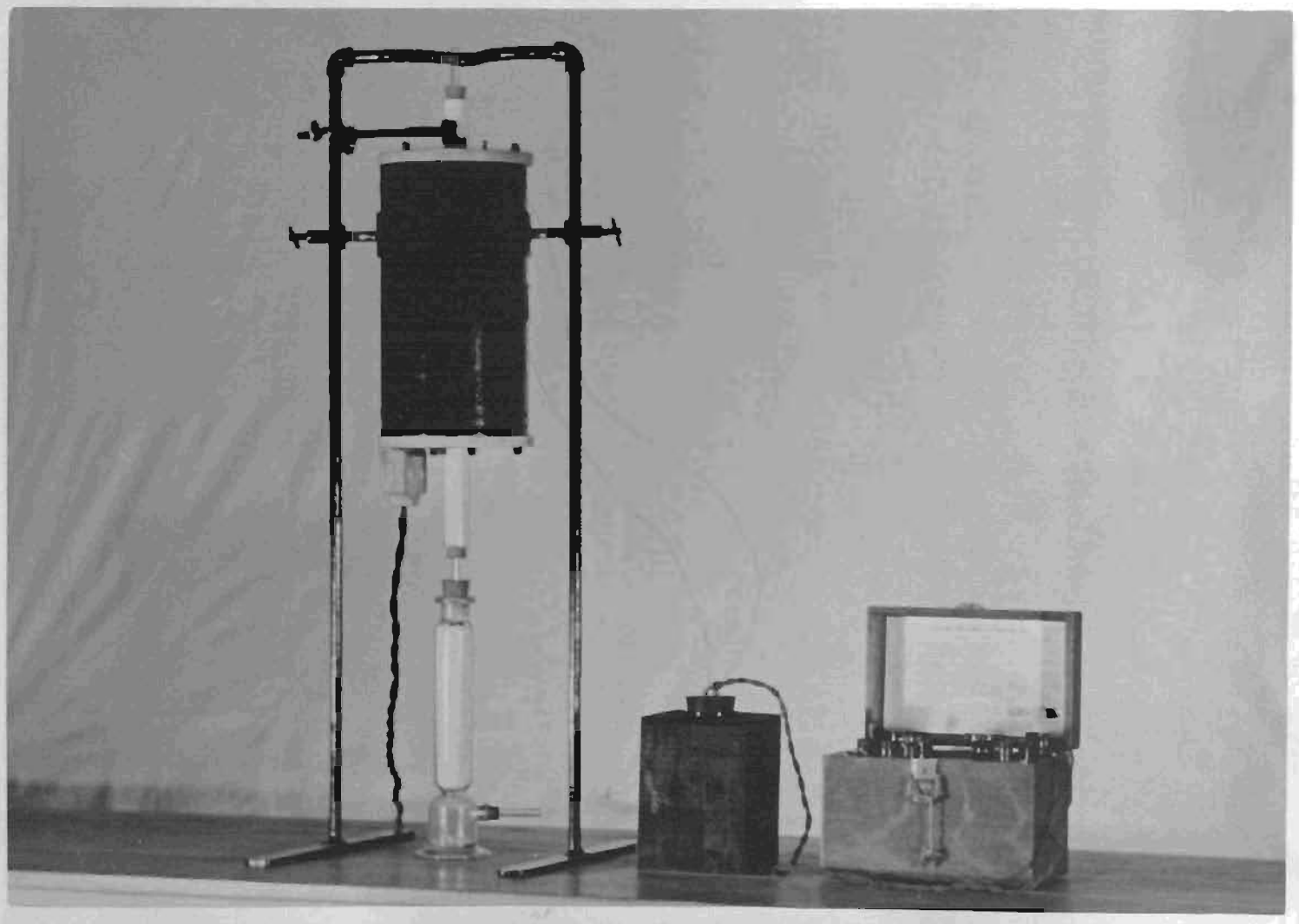

Figure 4. The Apparatus Assembled for Activation of a Catalyst.

## OPERATION

In the performance of a given experiment, the catalyst was first charged into the reaction tube and activated for twelve hours at 175° C. 100 ml. of catalyst, the quantity always used, was measured out in a graduated cylinder (see Fig. 4).

Known quantities of benzene or toluene, and water were then placed in their respective reservoirs along with several glass beads. Then the flasks were weighed and assembled into the apparatus as shown in Figure 2.

When the reaction tube was heated to the temperature desired, the heater beneath the water reservoir was turned on and the water brought to a boil. At this point the glass stop-cock in the tube connecting both reservoirs was turned off in order to prevent water from backin up into the benzene flask. The water flask was allowed to boil alone for several minutes in order to sweep out the reaction tube with steam. When drops of water began to collect in the receiving flask, the benzene was heated to boiling, and the vapors allowed to bubble through the boiling water, and finally to pass with the steam into the reaction tube.

The boiling rate of the two reservoirs was regulated independently by means of a slide wire rheostat connected in series with the heater beneath each flask. These rheostats were regulated so as to provide a slow steady boiling rate for each liquid, and were set in the same relative positions in each experiment. Because the current supply was quite irregular, the rate of vaporization for the two liquids varied from one experiment to another, and constituted

one of the least controlled factors in the experiments.

At the conclusion of an experiment the contents of both reservoirs, and also the reaction products in the receiving flask were weighed. The reaction products were separated into two components, an aqueous layer and an oily layer. The weight of each of these layers was then determined, and both were set aside for analysis.

Throughout the course of an experiment the furnace temperature fluctuated. This, of course, was greatest at the higher temperatures, and least at the lower temperatures. In order to arrive at a representative temperature for a given experiment, readings were taken every five minutes. At the end, these readings were averaged, and the resulting figure recorded as the temperature of the experiment.

## ANALYTICAL PROCEDURE

The quantitative determination of the hydrolysis reaction products (phenol, methanol, cresol, and benzyl alcohol) was found to be a difficult task. Fractional distillation proved of no value due to the minute quantities of products themselves and due to the presence of numerous pyrolysis products formed as the result of thermal decomposition of the benzene or toluene at the high temperatures employed in the experiments.[25] However, a scheme of analysis was eventually worked out which proved fairly reliable.

The oily layer of the reaction product was extracted with 100 ml. of 20% sodium hydroxide solution with vigorous agitation in a separatory funnel using 25 ml. at a time. The caustic layer was drawn off and combined with the aqueous layer of the reaction product. This solution was placed in a distilling flask and the first 30 ml. of distillate was collected and set aside. This fraction was later tested for methanol.

When the first 30 ml. of distillate had been collected, the distillation was stopped, the solution cooled and neutralized with glacial acetic acid, and filtered. The filtrate was vigorously agitated in a separatory funnel with about 5 ml. of bromine,[26] then drawn off into a beaker, and the precipitated tri-bromo phenol bromide allowed to coagulate and settle for 24 hours.

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25. Egloff, Gustav., The Reactions of Pure Hydrocarbons. New York, N. Y., Reinhold Publishing Corp., 1937, p. 498-541.

26. Kolthoff, I.M., De Analytische Toepassing Der Broomsubstitutie in Phenolen. Pharm. Weekbald, Vol. 69, p. 1147-1158, 1932.

The precipitate was filtered and collected in a fritted glass Jena crucible (fine porosity) and washed several times with very dilute bromine water. The crucible was finally placed in a vacuum dessicator over anhydrous calcium chloride and dried to constant weight; weighings were made every 24 hours.

This product was identified on several occasions as tri-bromo phenol bromide by reduction with sodium acid sulfite solution, to the tri-bromo phenol. The melting point of this compound, after recrystallization from 40% alcohol solution, checked favorably with that of tri-bromo phenol prepared from phenol in the laboratory.

The 30 ml. of distillate previously mentioned was tested qualitatively for methanol by placing 5 ml. in a test tube and oxidizing the solution three times with a heated copper spiral.[27] The solution was cooled after each operation. Two drops of a 0.5% solution of resorcinol was then added and the mixture poured gently down the side of an inclined test tube containing 5 ml. of concentrated sulfuric acid. The tube was rotated gently so as not to cause the disappearance of the two layers. A red flocculent precipitate at the junction of the layers is a test for methanol. This test for methanol was found to be accurate in dilutions as great as 1:1000 when the liquid is allowed to stand for 24 hours or longer. In no case, however, was any methanol detected in the reaction products of the experiments.

Cresol, another possible hydrolysis product, which would follow the separation of phenol, was never in evidence.

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27. Mulliken, S.P., A Method for the Identification of Pure Organic Compounds., New York, N. Y., John Wiley & Sons, 1904-1922, Vol. 1, p. 24 & 171.

The analysis of benzyl alcohol proved inconclusive. The oily layer of the reaction product from a number of experiments was fractionated and in each case no detectable quantities of this compound were obtained. Practically all methods for the identification of benzyl alcohol depend upon its oxidation to benzoic acid, which is very likely present due to the oxidation of small quantities of toluene during an experiment.[28] Therefore even though benzyl alcohol were identified by one of the usual methods there would be no indication as to whether its source had been the hydrolysis or the oxidation of toluene. The analysis of this compound was therefore abandoned.

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28. Parks, G.W., & Katz, J., Vapor-phase Catalytic Oxidation of Organic Compounds. Ind. & Eng. Chem., Vol. 28, p. 319-323, 1936.

## RESULTS

The data taken during this investigation has been classified into three different tables, according to the catalyst employed and the substance hydrolyzed. The time given refers to the duration of the experiment in minutes, and the temperature is the average temperature of the furnace during the experiment.

In all of the experiments with the exception of number five, 200 grams of benzene or toluene and 400 grams of water were placed in their respective reservoirs at the start. These quantities were reversed in experiment five, that is, 200 grams of water and 400 grams of toluene were the amounts used. The quantities of the reactants actually used up during an experiment are given in the fifth and sixth columns under Materials Used.

Table 2 gives the results of ten different experiments in which silica gels were used as catalysts with toluene and steam as reactants. The symbol in parenthesis in experiments 9 and 10, under catalysts, refer to the metallic salt used as a precipitating agent in the preparation of those two silica gels.[29] The same charge of catalyst was used over and over in each of the four experiments with ferric oxide silica gel. During an experiment the gel became fouled with carbon deposits; this was burned off and the gel reactivated by passing dry air through the gel mass at 500° C. for 12 hours. This restores the original color of the catalyst, and also the catalytic activity, which is verified by the results.

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29. See page 11.

Table 3 shows results of eight additional experiments with toluene and steam, using three other types of catalysts: activated alumina, magnetic oxide of iron, and cast iron drillings. These catalysts were discarded after each experiment. Variation in temperatures in the case of the iron catalyst and alumina catalyst show the effect of this variable on the phenol yield.

Table 4 gives data for four experiments with benzene and steam; activated alumina, and cast iron drillings being used as catalysts. Fresh quantities of catalyst were used for each experiment.

The terms nil, and trace as used in the tables convey the following meanings:-

Nil: no visible amount.

Trace: visible amount, but too small to weigh.

TABLE 2

THE HYDROLYSIS OF TOLUENE WITH SILICA GEL CATALYSTS

| No. | Time min. | Temp. °C. | Catalyst | Materials Used Toluene grams | Materials Used Water grams | Rate of Flow of Reactants Toluene g./min. | Rate of Flow of Reactants Water g./min. |
|---|---|---|---|---|---|---|---|
| 1 | 95 | 440 | Nickel Oxide Silica Gel. | 198.0 | 308.0 | 2.08 | 3.24 |
| 2 | 76 | 485 | Ferric Oxide Silica Gel. | 185.3 | 273.8 | 2.47 | 3.65 |
| 3 | 60 | 580 | Ferric Oxide Silica Gel. | 200.0 | 330.3 | 3.34 | 5.50 |
| 4 | 80 | 225 | Ferric Oxide Silica Gel. | 143.0 | 392.9 | 1.79 | 4.90 |
| 5 | 95 | 620 | Ferric Oxide Silica Gel. | 388.0 | 160.0 | 4.08 | 1.68 |
| 6 | 120 | 640 | Copper Oxide Silica Gel. | 174.0 | 376.5 | 1.45 | 3.13 |
| 7 | 65 | 595 | Cobalt Oxide Silica Gel. | 192.6 | 362.2 | 2.96 | 5.57 |
| 8 | 90 | 615 | Copper Silica Gel. | 182.2 | 386.7 | 2.02 | 4.29 |
| 9 | 75 | 450 | Pure (Ni) Silica Gel. | 184.0 | 281.0 | 2.46 | 3.75 |
| 10 | 60 | 480 | Pure (Fe) Silica Gel. | 191.0 | 270.8 | 3.18 | 4.52 |

TABLE 2

THE HYDROLYSIS OF TOLUENE WITH SILICA GEL CATALYSTS

| No. | Products: Oil Layer grams | Products: Water Layer grams | Moles of Water per mole of Toluene | Tri-bromo phenol bromide grams | Phenol Equiv-alent grams | grams Phenol per 1000 grams of Toluene |
|---|---|---|---|---|---|---|
| 1 | 193.7 | 300.6 | 7.49 | 0.0240 | 0.0055 | 0.0277 |
| 2 | 182.2 | 265.0 | 7.56 | 0.0136 | 0.0032 | 0.0170 |
| 3 | 198.2 | 320.1 | 8.43 | 0.0355 | 0.0083 | 0.0415 |
| 4 | 139.7 | 382.6 | 13.69 | 0.0278 | 0.0063 | 0.0444 |
| 5 | 375.0 | 155.0 | 4.40 | Nil. | ------ | ------ |
| 6 | 168.2 | 386.6 | 11.08 | 0.0432 | 0.0099 | 0.0568 |
| 7 | 182.3 | 358.4 | 9.61 | 0.0100 | 0.0023 | 0.0119 |
| 8 | 178.7 | 384.9 | 10.90 | 0.0114 | 0.0026 | 0.0143 |
| 9 | 181.0 | 274.2 | 7.80 | 0.0007 | 0.0002 | 0.0009 |
| 10 | 189.8 | 261.8 | 7.29 | Nil. | ------ | ------ |

TABLE 3

THE HYDROLYSIS OF TOLUENE WITH OTHER CATALYSTS

| No. | Time min. | Temp. °C. | Catalyst | Materials Used Toluene grams | Water grams | Rate of Flow of Reactants g./min. | g./min. |
|---|---|---|---|---|---|---|---|
| 11 | 70 | 615 | Activated Alumina. | 195.8 | 252.0 | 2.80 | 3.60 |
| 12 | 80 | 775 | Activated Alumina. | 189.0 | 310.0 | 2.36 | 3.88 |
| 13 | 70 | 245 | Activated Alumina. | 193.0 | 218.5 | 2.78 | 3.12 |
| 14 | 85 | 620 | $Fe_3O_4$ | 188.2 | 342.7 | 2.21 | 4.03 |
| 15 | 70 | 390 | Cast Iron Drillings. | 198.5 | 322.7 | 2.83 | 4.61 |
| 16 | 60 | 590 | Cast Iron Drillings. | 189.5 | 315.7 | 3.15 | 5.62 |
| 17 | 120 | 635 | Cast Iron Drillings. | 136.0 | 396.3 | 1.13 | 3.30 |
| 18 | 105 | 920 | Cast Iron Drillings. | 173.7 | 393.6 | 1.65 | 3.74 |

TABLE 3

THE HYDROLYSIS OF TOLUENE WITH OTHER CATALYSTS

| No. | Products: Oil Layer grams | Products: Water Layer grams | Moles of Water per mole of Toluene | Tribromo phenol bromide grams | Phenol Equivalent grams | grams Phenol per 1000 grams of Toluene |
|---|---|---|---|---|---|---|
| 11 | 191.0 | 251.7 | 6.60 | Trace | ------ | ------ |
| 12 | 174.0 | 274.5 | 8.40 | 0.0243 | 0.0056 | 0.0294 |
| 13 | 190.5 | 210.7 | 5.80 | Nil. | ------ | ------ |
| 14 | 181.0 | 351.6 | 9.34 | 0.0302 | 0.0069 | 0.0367 |
| 15 | 195.7 | 317.8 | 8.10 | Trace | ------ | ------ |
| 16 | 187.8 | 303.3 | 8.51 | 0.0047 | 0.0011 | 0.0056 |
| 17 | 130.9 | 576.7 | 14.86 | 0.1332 | 0.0259 | 0.1905 |
| 18 | 159.9 | 332.2 | 11.60 | 0.3106 | 0.0711 | 0.4029 |

TABLE 4

THE HYDROLYSIS OF BENZENE

| No. | Time min. | Temp. °C. | Catalyst | Materials Used Benzene grams | Water grams | Rate of Flow of Reactants g./min. | g./min. |
|---|---|---|---|---|---|---|---|
| 19 | 40 | 680 | Activated Alumina. | 197.4 | 239.4 | 4.94 | 5.98 |
| 20 | 60 | 360 | Cast Iron Drillings. | 198.1 | 294.1 | 3.30 | 4.90 |
| 21 | 65 | 605 | Cast Iron Drillings. | 199.6 | 357.5 | 2.85 | 5.10 |
| 22 | 65 | 860 | Cast Iron Drillings. | 198.3 | 328.9 | 3.05 | 5.06 |

TABLE 4

THE HYDROLYSIS OF BENZENE

| No. | Products: Oil Layer grams | Products: Water Layer grams | Moles of Water per mole of Benzene | Tribromo phenol bromide grams | Phenol Equivalent grams | grams Phenol per 1000 grams of Benzene |
|---|---|---|---|---|---|---|
| 19 | 227.2 | 296.9 | 5.24 | Trace | ------ | ------ |
| 20 | 195.8 | 287.2 | 6.42 | Nil | ------ | ------ |
| 21 | 193.2 | 342.5 | 7.75 | 0.0113 | 0.0026 | 0.0129 |
| 22 | 163.2 | 283.0 | 7.18 | 0.7696 | 0.1762 | 0.8899 |

## DISCUSSION

In the course of this investigation it became apparent that three variables were controlling the phenol yield: the catalyst, the temperature, and the molar ratio of water to benzene or toluene. The tables, therefore, can be interpreted to show the effect of each of these variables.

Experiments 9, and 10 show that the pure silica type catalysts are relatively ineffective as compared with the metal oxide impregnated type of silica gel. The yield of phenol in experiment 9 was extremely low while that in experiment 10 was nil.

It is difficult to say which of the metal oxide gels was best due to the variable temperatures, and to the variable molecular ratio of toluene to water. These factors varied considerably from one experiment to another. However, a comparison of the results in experiments 1, 3, and 6 indicates that nickel oxide, iron oxide and copper oxide impregnated gels are about equally effective.

| No. | Temp. °C. | Catalyst | Moles of Water per mole of Toluene | grams Phenol per 1000 grams Toluene |
|---|---|---|---|---|
| 1 | 440 | Nickel Oxide Silica Gel. | 7.49 | 0.0277 |
| 3 | 580 | Ferric Oxide Silica Gel. | 8.43 | 0.0415 |
| 6 | 620 | Copper Oxide Silica Gel. | 11.08 | 0.0568 |

Experiments 3, 4, and 5, each using Ferric Oxide Silica Gel, show very clearly the effect of changing the molecular ratio of water to toluene. The largest yield was obtained in experiment

4, in which the amount of water used was in excess of 13 times the theoretical amount necessary. In experiment 5 the amount of water was only 4 times the theoretical amount and the yield was nil. This shows that the contention of Fischer, Schrader, and Meyer[30] regarding the shift in equilibrium due to excess water in the hydrolysis of benzene, also applies to toluene.

| No. | Temp. °C. | Moles of Water per mole of Toluene | grams Phenol per 1000 grams Toluene |
|---|---|---|---|
| 5 | 620 | 4.40 | Nil. |
| 3 | 580 | 8.43 | 0.0415 |
| 4 | 225 | 13.69 | 0.0444 |

It was discovered on completion of experiment 6 that the copper oxide gel catalyst had undergone reduction to metallic copper. Experiment 8 was carried out to determine the effect of a stable copper gel catalyst. This catalyst was prepared by activating copper oxide silica gel with hydrogen for 12 hours at 500° C. Results show that the copper oxide gel was the better of the two.

Activated alumina was found to be even less effective than the pure silica gel catalysts. Experiment 12 shows that a temperature in excess of 700° C. was necessary for detectable yields of phenol. Cast iron drillings on the other hand was found to be the most effective catalyst used in the entire investigation.

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30. Fischer, Franz., Schrader, Hans., & Meyer, Wilhelm. Über die Thermische Behandlung Aromatischer Verbindungen (II Teil). Ges. Abhandl. Kenntn. Kohle., Vol. 5, p. 417-419, 1920.

Experiments 15, 16, 17, and 18 show that an increase in temperature effects an increase in the phenol yield using that catalyst.

| No. | Temp. °C. | Moles of Water per mole of Toluene | grams Phenol per 1000 grams Toluene |
|---|---|---|---|
| 15 | 390 | 8.10 | Trace |
| 16 | 590 | 8.51 | 0.0056 |
| 17 | 635 | 14.86 | 0.1905 |
| 18 | 920 | 11.60 | 0.4029 |

Due to reaction with steam, the cast iron catalyst became oxidized during an experiment with the evolution of hydrogen. In order to determine whether or not this was desirable, experiment 14 was conducted using oxidized cast iron drillings as the catalyst.[31] Results show it to be less effective than the unoxidized iron.

Experiments 19, 20, 21, and 22 were carried out with benzene instead of toluene. The results show that cast iron drillings was the superior catalyst of the two used, and that the phenol yield was effected by temperature exactly as in the case of toluene.

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31. See page 12.

## CONCLUSIONS

### (Toluene)

It has been found possible to hydrolyze toluene to phenol to the extent of 0.4 gram per 1000 grams of toluene, by passing toluene vapor mixed with steam over cast iron drillings at 900° C.

The ability to catalyze the hydrolysis was possessed by a number of catalysts; cast iron drillings, activated alumina, magnetic oxide of iron, metal oxide impregnated silica gels, and pure silica gels.

Pure silica gels and activated alumina showed little activity.

Cast iron drillings appeared to be the most active catalyst.

With cast iron drillings as the catalyst the reaction proceeded at measurable speed at 400° C. and above.

No detectable amounts of phenol were obtained when the amount of water was less than four times the theoretical amount necessary.

### (Benzene)

It was possible to hydrolyze benzene to phenol to the extent of 0.8 gram per 1000 grams of benzene, by passing benzene vapor mixed with steam over cast iron drillings at 900° C.

With cast iron drillings as the catalyst the reaction proceeded at measurable speed at 400° C. and above.

Activated alumina showed little or no activity.

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